RECENT INNOVATIVE TECHNOLOGIES FOR CATALYTIC DECOMPOSITION OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN AIR STREAM

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ABSTRACT

This article presents recent researches done in developing new and innovative technologies for VOCs catalytic decomposition. The quest for ideal catalyst formulations and three types of new catalytic reactor systems, viz. reverse-flow reactor, adsorption-catalytic reactor and photocatalytic reactor are discussed. Reverse-flow reactor employs a periodic reversal of the feed gas flow to operate the reactor under unsteady-state condition. Better distribution of heat across the catalyst bed and a more economical operation of a fixed-bed catalytic reactor are expected. Proper attention however, should be given to avoiding the occurrence of hot spots. Ad-Cat technology refers to an adsorption process complemented by a catalytic decomposition of the VOCs. A more efficient treatment and economically viable VOC abatement system is expected using this combined processes. Photocatalytic system is another innovative technology currently under investigation to materialize VOC decomposition at at near ambient temperature by the use of semiconductor catalysts and the presence of UV or near UV-lights.

Keywords : VOC, catalyst, reverse-flow, Ad-Cat, photocatalytic.

INTRODUCTION

Volatile organic compounds (VOCs) are air pollutants which are emitted from many industrial processes [1] and transportation activities [2]. Catalytic combustion is one of the most promising technology for the decomposition of VOCs due to its definitive character and saving of energy [3]. Typically, the reaction temperature is in the range of 150° to 480°C [4] and is determined on the basis of the material being oxidized

THE CATALYST FORMULATION

Table 1: Recent catalyst compositions being studied for VOC total oxidation.

Reference	Reaction conditions			Remarks
	VOC	Catalyst	Temperature	
[5]	CFC113	Pd & W/TiO_2-ZrO_2	300°-500°C	High conversion of CFC113 (>95%) but CO significantly detected in product gas. No significant deactivation detected after 150 hrs of time-on-stream.
[2]	Benzene, toluene & xylene	Cu-Y & Pd-Y zeolites	220°-350°C	Pd-Y more active while Cu-Y was active only at higher Cu loading. Complete oxidation reported.
[6]	Hexane, toluene, benzene & isooctane.	Rh/Al_2O_3 & $Rh/CeO_2/Al_2O_3$	100°-400°C	Ease of total oxidation is hexane<toluene<benzene<isooctane. Addition of CeO_2 improved activity.
[7]	*o*-xylene	Pd-FAU zeolites	150°-330°C	Coke retention in the pores at low temperatures. Activity increases with Pd content.
[8]	Methane, chloromethane & dichloromethane	$LaMnO_3$ & $LaCoO_3$ perovskites (on monolith)	300°-600°C	Mechanically stable and catalytically active for total oxidation of VOCs. $LaCoO_3$ irreversibly deactivated. High chlorinated by-products in the outlet gas.

Table 1 summarizes some recent researches on developing catalyst for VOC decomposition. Supported metal catalysts are no doubt, one of the most actively researched materials. Current trend is to achieve further improvement of the catalytic system such as by incorporating CeO_2 as an oxygen storage component [6], combination of support materials and deliberate inclusion of water in the feed stream for certain applications [5]. Perovskite catalysts are the preferred catalysts for high temperature operation [8] as they exhibit excellent thermal stability. Problems of deactivation and poor selectivity for deep decomposition products are two of the most significant problems associated with these two group of catalysts.

Metal-exchanged zeolites have wide potential as they can be formulated to carry active metal catalysts through metal exchange procedure to give near molecular level metal dispersion [9]. This property, coupled with the size and shape features of the zeolites, allow the materials to be used as catalysts in extremely selective reactions. The following systems have been investigated : Cu-Y and Pd-Y/benzene [2], Pd-siliceous Y/hexane [10] and Pd/HFAU/*o*-xylene [7] and the results are very promising. Problem of catalyst deactivation due to chlorinated species in the feed stream is however not fully solved. Another major challenge is to suppress the formation of higher chlorinated species and improve selectivity toward deep oxidation products.

REACTOR SYSTEM

1) Reverse-flow reactor

The catalytic reverse-flow process emerged as a new type of catalytic process featuring periodic reversal of the gas flow direction through a packed bed catalyst [11]. The principal diagram of reverse-flow reactor is as depicted in Figure 1. In a reverse-flow reactor, the catalyst bed serves not only to accelerate the chemical reaction but also as a heat exchange and heat accumulation media [12].

Figure 2 depicts the typical profiles of axial temperature and conversion in a reverse-flow reactor. It consists of three clear regime i.e. heating, stabilized and cooling. The conversion is normally significant beginning from the upper part of the catalyst bed. The profiles have a nearly constant shape during the large part of the reactor. Table 2 presents several successful application of the reverse-flow reactor for VOC catalytic decomposition where the removal efficiency is between 95 % to 99 % depending on the operational variables

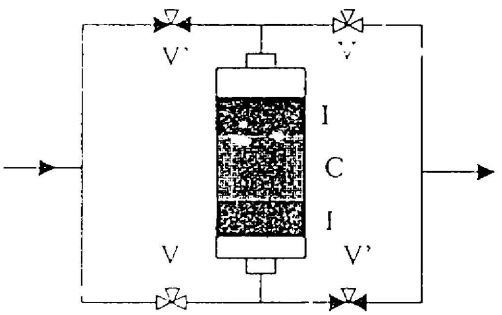

Figure 1: Principal diagram of reverse-flow reactor : V and V', switching valves; C, catalyst bed, I, inert material [13].

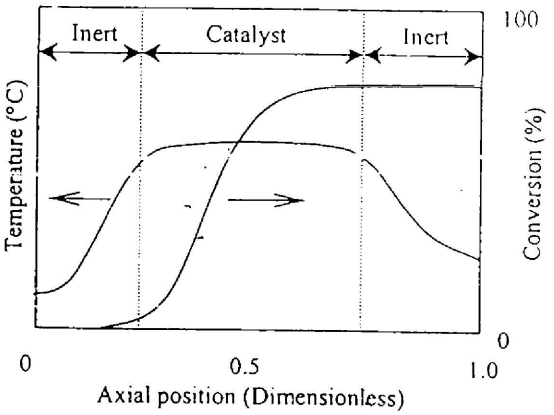

Figure 2 : Profiles of typical axial temperature and conversion in a reverse-flow reactor.

Table 2 : Gas purification using catalytic reverse-flow reactor [13].

VOC	Concentration (g/m^3)	Flow rate (m^3/hr)	Temperature (°C)		Cycle duration (min)	Removal efficiency (%)
			Inlet	Maximum		
C_1-C_5 alcohols	0.5-0.7	600-800	20-60	400-700	22-55	99.0-99.6
2-ethylhexanol	0.1-1.5	800	40-50	400-450	14-45	97.0
Methanol, phenol & formaldehyde	0.5-0.7	650	15-20	500-650	30-45	98-99
Acrylonitrile, cyanic acid & acetaldehyde	1.0-5.5	2000-5500	10-60	520-700	11-25	95-99

Reverse-flow reactors are susceptible to hot spot formation that must be properly controlled [14]. The hot spots are, quite often, very localized and difficult to cool and excessive cooling would extinguish the reactor entirely. Keith et al. [12] proposed the enhanced thermal dispersion unit using embedded steel rods and wires in an optimal configuration within the bed. Besides, the dilution of the feed stream with extra air can also be used to control the bed temperature [14].

2) Ad-Cat technology

The presence of VOC pollutants in air is normally featured by high-volume/low-concentration. To cope with this situation, it is feasible to establish a combined adsorption/catalytic decomposition (Ad-Cat) process [15]. It refers to an adsorption process complemented by a catalytic decomposition step to ultimately diminish the concentrated pollutant stream produced during the regeneration step. It can either be operated using the same dual-function sorbent/catalyst bed [16, 17] or the adsorption and catalysis decomposition are done separately [15].

Figure 3 presents typical reactor configurations that can be used for Ad-Cat process study. Figure 3(a) employs periodical heating i.e. after the occurrence of adsorption breakthrough in the adsorption process. In this type of reactor, the mode of operation is purely cyclical [18]. Major weakness in this configuration is, as the furnace heats up, the adsorbed VOC will gradually be released from the adsorbent but before the temperature reaches sufficiently high value to initiate catalytic reaction, small portion of the VOC will escape unreacted. Atwood et al. [16] used a reactor as depicted in Figure 3(b) to curb this problem. The sufficiently heated furnace is gradually lowered after the sorbent/catalyst has saturated with VOC and the initial positions of the furnace, relative to the top level of the catalyst bed was studied as the operation variables. A concept of fixed-bed adsorption-catalytic reverse-process (Figure 3(c)) was introduced by Zagoruiko et al. [19]. They reported high purification efficiency of more than 99.9 % with extremely low energy consumption of less than 1-3 kJ/m^3 of VOC contaminated air processed. However, for processing of continuous flow air stream, major modification still need to be done on this configuration.

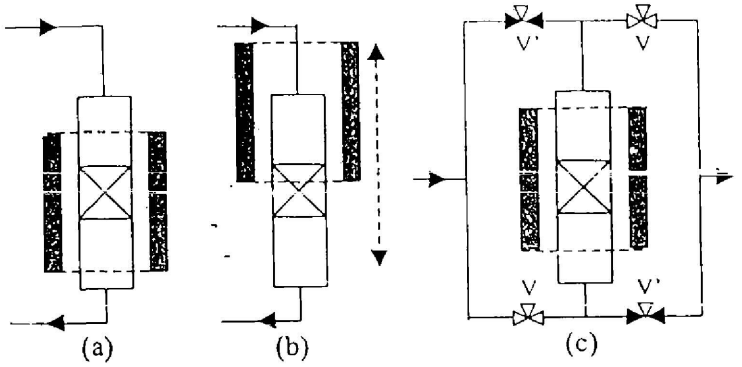

Figure 3 : Several reactor set-up for adsorption-catalytic decomposition process study. a) fixed-bed with periodical heating, b) falling furnace reactor, c) fixed-bed adsorption-catalytic reverse-process (V and V' = switching valves).

Activated carbon is the most widely used adsorbent for trapping VOCs (Table 3). Other alternative materials recently under evaluation are such as activated carbon fiber (ACF) [15] and hydrophobic zeolites [18]. Activated carbon fiber has some advantages over granular or powdered activated carbon material as the thin fiber shape assures fast interparticle adsorption kinetics compared with other activated carbon particles.

Table 3 : Review of recent researches on Ad-Cat technology.

Reference	Sorbent/Catalyst	VOC	Remarks
[18]	Cr-ZSM-5 (dual-function)	TCE	TCE saturation capacity increased with SiO_2/Al_2O_3 ratio of ZSM-5. SiO_2/Al_2O_3 ratio of 80 gives preferred performance of dual-function sorbent/catalyst.
[16]	Cr-ZSM-5 (dual-function)	TCE	Greater than 99% destruction was achieved. 80%-90% energy savings were demonstrated.
[15]	Activated carbon fibre (sorbent) Cr_2O_3/TiO_2 (catalyst)	o-dichloro benzene	Complete decomposition achieved at 300°C and GHSV of 15,000hr^{-1}. Heating energy is saved by about 40 times.
[17]	Catalytically modified activated carbon (dual-function)	Methyl bromide & methyl iodide	Methyl bromide and methyl iodide were strongly adsorbed on the activated carbon. Decomposition increased in humid condition.

3) Photocatalytic technology

Gas phase heterogeneous photocatalytic oxidation (PCO) is a relatively recent technology which is being investigated for its potential use in removing VOCs from air streams [20]. It allows the oxidation of airborne VOCs into carbon dioxide and water at near room temperature in the presence of a semiconductor catalysts (e.g. TiO_2) and UV, or near-UV light source. When the catalyst absorbs photons having greater energy than the band gap of the semiconductor, electrons are excited from the valence to the conduction band leaving holes behind. The resulting electron-hole pairs can migrate towards the catalyst surface and initiate redox reaction that oxidize the adsorbed organic [21].

Figure 4 presents the schematic diagram of a typical reactor for photocatalytic degradation of VOC study. The reactor is often made from transparent materials such as quartz [21] or an opaque material with transparent window [22] to allow the penetration of UV-light. Heterogenous photocatalysis has been shown (Table 4) to oxidize a broad range of contaminants including oxygenate [23], aromatic [21] and chlorinated VOCs [24].

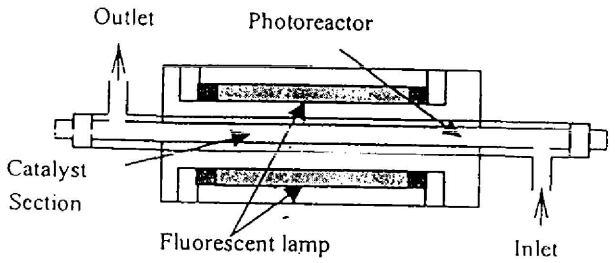

Figure 4 : Schematic diagram of a typical reactor used for photocatalysis study.

Attractive advantages with photocatalysis for air treatment and purification are : near ambient temperature and pressure operation (mild conditions); use of atmospheric oxygen as the oxidant; and final oxidation products with higher mineralization fraction [22]. Gaseous heterogeneous photocatalytic oxidation has been demonstrated as an efficient abatement technology for destruction of aromatic compounds, halocarbons, alcohols etc. Photocatalytic decomposition can also be combined with high temperature operation to further improve its efficiency [25].

Table 4 : Review of recent VOC photocatalytic decomposition studies.

Reference	Experimental conditions			Observation/Remarks
	VOC	Catalyst	Light	
[22]	Toluene & TCE	Pt & V_2O_5/TiO_2 (Monolithic)	1-10 Wcm^{-2} (Photon flux) 300-400 nm	Doping with Pt & V_2O_5 increases TCE conversion. TCE decomposition seems to proceed via a Cl• radical initiated mechanism.
[24]	TCE	TiO_2	365 nm	H_2O decreases photoactivity. Reaction rate increases with higher flow rate and light intensity.
[25]	TCE	TiO_2 (Monolithic)	UV region (Temperature 60°-250°C)	Reactions involving chlorine radicals were not improved by an increase in temperature. Dechlorination of by-products detected.
[21]	Toluene	TiO_2	UV region	Smaller particle sizes show better selectivity to for total mineralization. H_2O must present to maintain catalyst reactivity.

Although Avila et al. [22] reported high selectivity toward complete mineralization products, the presence of by-products in the product gas was still significant. In fact, most of the researchers reported the presence of higher by-products such as acetaldehyde and ethyl acetate from ethanol and diethyl ether respectively [26], highly toxic phosgene from TCE and chloroform [27], and benzaldehyde from toluene [21]. In addition to that, competitive adsorption of water on the surface of the catalyst is found to bring about adverse effect on the reaction in TCE/TiO_2 system [24]. Avila et al. [24] in their study concluded that the degree of complete mineralization is actually strongly dependent on the type of the compound to be removed.

CONCLUSION

Most of the successful research works on VOCs total catalytic decomposition employ either noble metals (Pt and Pd), metal oxides (Cr, Co, Cu, Fe, Mn and V) or mixed oxides (perovskites). Zeolite-based catalysts are currently being evaluated as they posses very high surface area and can provide high metal dispersion beside demonstrating high thermal stability and selectivity for deep decomposition products. In a reverse-flow reactor, reversing the feed gas flow will create unsteady-state condition

across the depth of the catalyst bed. Better distribution of heat and a more economical operation of a fixed-bed catalytic reactor is the likely consequence. Combined adsorption and catalytic decomposition of VOCs (Ad-Cat) can offer a more efficient treatment and economically viable VOC abatement system. Photocatalytic system is a technology currently under serious investigation to achieve VOC decomposition even at lower operating temperature. By the use of a semiconductor catalysts and the presence of UV or near UV-lights, deep oxidation of VOCs can be materialized at near ambient temperature.

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